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Reaction of 2,3-Dialkylaziridines with Carbon Disulfide

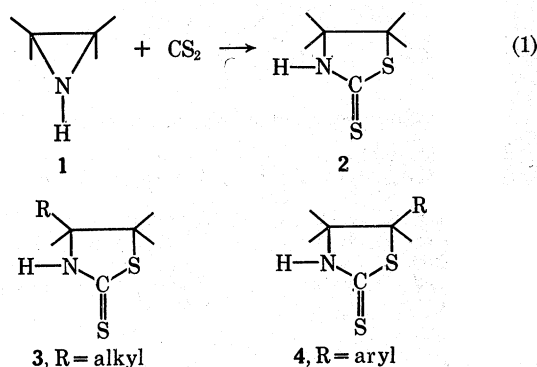
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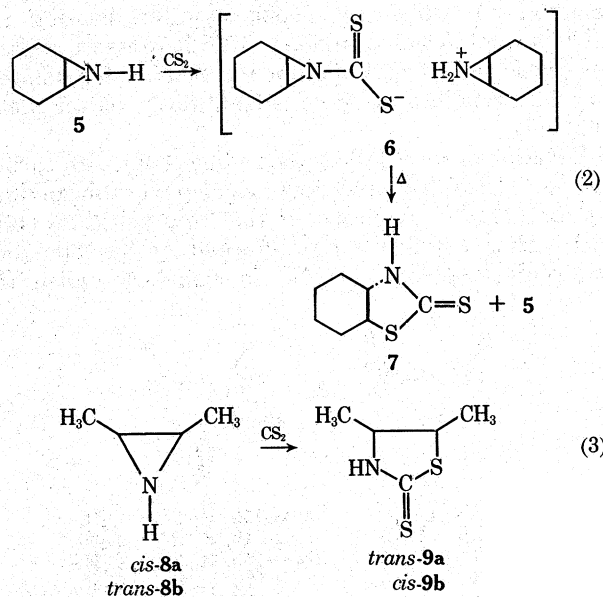
The reaction of *cis*- and *trans*-2,3-dialkyl-substituted aziridines with carbon disulfide to yield 4,5-disubstituted thiazolidine-2-thiones has been studied. The yields of the thiazolidinethiones are in the range of 30–80%. The geometric configurations of the thiazolidinethiones have been elucidated by means of nmr and mass spectroscopy. It has been found that the thiazolidinethiones have the opposite geometry as the starting aziridines. Starting with a *cis*-aziridine yields a *trans*-thiazolidinethione, while the *trans*-aziridine yields the corresponding *cis*-thiazolidinethione. The reaction has been determined to be stereospecific for *cis*-aziridines but only stereoselective for *trans*-aziridines. Also studied was the reaction of 2-alkyl-substituted aziridines with carbon disulfide. The products from this reaction were found to be 4-alkyl-substituted thiazolidine-2-thiones.

The reaction of ethylenimine (1) with carbon disulfide to give thiazolidine-2-thiones (2) (eq 1) was initially



reported by Gabriel, *et al.*^{1,2} The scope of this reaction was later extended by Clapp, *et al.*,³ to include alkyl-substituted ethylenimines. These authors found that the reaction of 2-alkylaziridines with carbon disulfide yielded the corresponding 4-alkylthiazolidine-2-thione derivatives (3), thus establishing that for alkyl-substituted aziridines the three-membered ring is opened preferentially at the least substituted carbon atom. Similar orientation results have also been observed with *N*-alkyl- and *N*-aryl-2-alkylaziridines.^{4,5} More recently, Kotera, *et al.*,⁶ utilized this reaction for the derivatization of a number of 2-aryl-substituted aziridines. The thiazolidine-2-thiones so prepared were described as the 5-substituted isomers (4), thus indicating that the aziridine ring had been opened at the position bearing the aryl substituent.

With cyclohexylimine (5) Winternitz, *et al.*,⁷ observed the formation of perhydrobenzo-4,5-thiazolidine-2-thione (7) whose stereochemistry about the ring junction was definitively assigned as *trans*. An isolated intermediate from this reaction was assigned the aziridinium dithiocarbamate structure 6 which was found to liberate the thiazolidinethione and cyclohexylimine on pyrolysis (eq 2). The stereochemical outcome of this reaction has also been suggested by Dewey, *et al.*,⁸ who studied this reaction with *cis*- and *trans*-2,3-dimethylaziridine (8a and 8b). The thiazolidine-2-thiones obtained from these aziridines were assigned the *trans* and *cis* geometry (9a and 9b), respectively (eq 3).



- (1) S. Gabriel and R. Stelzner, *Chem. Ber.*, **28**, 2929 (1895).
- (2) S. Gabriel and C. F. von Hirsch, *ibid.*, **29**, 2747 (1896).
- (3) L. B. Clapp and J. W. Watjen, *J. Amer. Chem. Soc.*, **75**, 1490 (1953).
- (4) V. I. Markov and S. I. Burmistrov, *Zh. Obshch. Khim.*, **35**, 162 (1965).
- (5) H. Stamm, *Pharm. Zentralh.*, **107**, 440 (1968).
- (6) K. Kotera, S. Miyazaki, H. Takahashi, T. Okada, and K. Kitahonoki, *Tetrahedron*, **24**, 3681 (1968).

- (7) F. Winternitz, M. Mouserron, and R. Dennilaule, *Bull. Soc. Chim. Fr.*, 1228 (1956).
- (8) C. S. Dewey and R. A. Bafford, *J. Org. Chem.*, **30**, 491 (1965).

However, the structural proof for these assignments was not rigorous.

In this present investigation we have undertaken a study of the reaction of a number of substituted aziridines with carbon disulfide to substantiate the stereochemical course of the reaction and to gain some insight into the mechanism of the reaction.

Results and Discussion

The present study concerns the addition reaction of carbon disulfide with *cis*- and *trans*-2,3-diethylaziridine (10a and 10b), *cis*- and *trans*-2,3-dioctylaziridine (14a and 14b), methyl *cis*-8-(3-octyl-2-aziridinyl)octanoate (16), and 2-octyl- and 2-decylaziridine (18 and 19). The yields of isolated analytically pure thiazolidine-2-thiones were in the range of 30–80% (Table I). Two

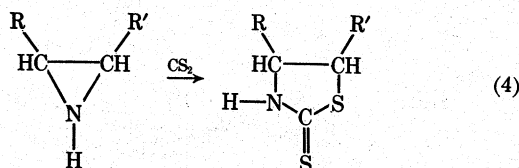
TABLE I
THIAZOLIDINE-2-THIONES

Compd ^a	R	R'	Stereochemistry	Yield, % ^b	
				Method A	Method B
11a	C ₂ H ₅	C ₂ H ₅	<i>trans</i>	44	64
11b	C ₂ H ₅	C ₂ H ₅	<i>cis</i>	38	61
15a	C ₈ H ₁₇	C ₈ H ₁₇	<i>trans</i>	36	59
15b	C ₈ H ₁₇	C ₈ H ₁₇	<i>cis</i>		83
17	C ₈ H ₁₇	C ₇ H ₁₅ CO ₂ CH ₃	<i>cis</i>	28	72
20	C ₈ H ₁₇	H		43	
21	C ₁₀ H ₂₁	H		39	

^a Satisfactory analytical values ($\pm 0.4\%$ for C, H, N, and S) were reported for all compounds in table: Ed. ^b Method A, reacting aziridine in refluxing CS₂; method B, reacting aziridine and CS₂ at 100°.

addition procedures were employed for the preparation of the thiazolidinethiones. One method involved reacting the aziridine in excess refluxing carbon disulfide (method A), while the second required heating the aziridine and carbon disulfide to 100° in pressure apparatus (method B) (see Experimental Section for details). The latter procedure gave substantially better yields (Table I).

Reaction of *cis*-2,3-diethylaziridine (10a) with carbon disulfide, by either procedure, yielded the thiazolidine-2-thione (11a). Reaction of the *trans*-aziridine (10b) with carbon disulfide at 100° afforded the corresponding thiazolidine-2-thione (11b). In contrast, when the

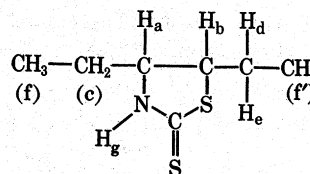


<i>cis</i> -10a, R, R' = C ₂ H ₅	<i>trans</i> -11a, R, R' = C ₂ H ₅
<i>trans</i> -10b, R, R' = C ₂ H ₅	<i>cis</i> -11b, R, R' = C ₂ H ₅
<i>cis</i> -14a, R, R' = C ₈ H ₁₇	<i>trans</i> -15a, R, R' = C ₈ H ₁₇
<i>trans</i> -14b, R, R' = C ₈ H ₁₇	<i>cis</i> -15b, R, R' = C ₈ H ₁₇
<i>cis</i> -16, R = C ₈ H ₁₇ , R' = C ₇ H ₁₅ CO ₂ CH ₃	<i>trans</i> -17, R or R' = C ₈ H ₁₇ , R or R' = C ₇ H ₁₅ CO ₂ CH ₃
18, R = C ₈ H ₁₇ ; R' = H	20, R = C ₈ H ₁₇ ; R' = H
19, R = C ₁₀ H ₂₁ ; R' = H	21, R = C ₁₀ H ₂₁ ; R' = H

reaction of 10b was carried out in refluxing carbon disulfide, no thiazolidinethione was isolated. Instead, an intermediate, assumed to have an aziridinium dithiocarbamate salt structure similar to that proposed by Winternitz, *et al.*,⁷ was isolated.

Reaction of 11a and 11b with *p*-nitrobenzoyl chloride yielded the corresponding 3-*p*-nitrobenzoyl derivatives as crystalline solids. The assignment of the *p*-nitrobenzoyl substituent to the 3 position of the thiazolidine-thione ring was confirmed by examination of the ir spectra^{3,8} of 11a and 11b.

Comparison of the nmr spectra of the thiazolidinethiones was quite informative in assigning the geometric configuration of 11a and 11b. A complete analysis of the spectra is given below. Of paramount importance are the observed methine coupling constants for protons H_a and H_b of the two isomers. In isomer 11a, this coupling is found to be 4.2 Hz while for 11b the magnitude of this coupling is 6.75 Hz. It is generally accepted that in five-membered heterocyclic ring systems, *cis*-methine coupling is generally larger than *trans*-methine coupling.^{9–11} Accordingly, a tentative assignment of geometric configuration for the respective isomers is that the thiazolidinethione 11a has the *trans* configuration, while isomer 11b has the *cis* configuration.



Nmr spectra of thiazolidine-2-thiones

<i>trans</i> -11a	<i>cis</i> -11b
H _a , δ 3.82 (dt, $J_{ab} = 4.2$, $J_{ac} = 6.0$ Hz)	4.12 (q, $J_{ab} = J_{ac} = 6.8$ Hz)
H _b , 3.50 (qd, $J_{ba} = 4.2$, $J_{bc} = 6.3$, $J_{bd} = 7.2$ Hz)	3.78 (qd, $J_{ba} = 6.8$, $J_{bc} = 5.3$, $J_{bd} = 9.0$ Hz)
H _{c-e} , 1.80 (m)	1.74 (m)
H _{f, f'} , 1.02 (t, $J = 6.8$ Hz)	1.02 (t), 0.98 (t, $J = 7.2$ Hz)
H _g , 8.88 (s)	8.82 (s)

Further support for the above assignments was provided by the mass spectral fragmentation patterns of 11a and 11b. Comparison of these spectra reveals that for thiazolidinethione 11b one observes a P – 2 ion which is not seen in the spectrum of 11a. Even more informative is the much more intense P – 29 ion observed in the spectrum of 11a in comparison with the spectrum of 11b. These variations are typical of the fragmentation patterns observed for the Δ^2 -oxazoline ring system¹² and therefore are in accord with the assigned stereochemistry of 11a and 11b (Figure 1).

Further proof of structure and stereochemistry for the thiazolidine-2-thiones 11a and 11b was obtained by their conversion to the corresponding 2-methylthio- Δ^2 -thiazoline derivatives. These transformations were

(9) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

(10) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, and references listed therein.

(11) (a) T. A. Foglia and D. Swern, *J. Org. Chem.*, **34**, 1680 (1969); (b) T. A. Foglia, L. M. Gregory, and G. Maerker, *ibid.*, **35**, 3779 (1970).

(12) S. Osman, C. J. Dooley, T. A. Foglia, and L. M. Gregory, *Org. Mass Spectrom.*, in press.

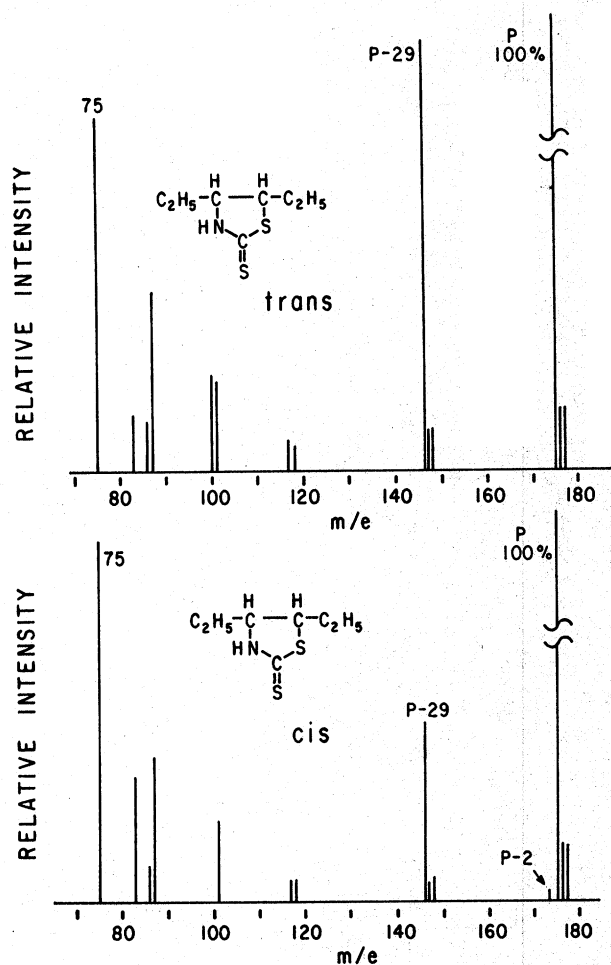
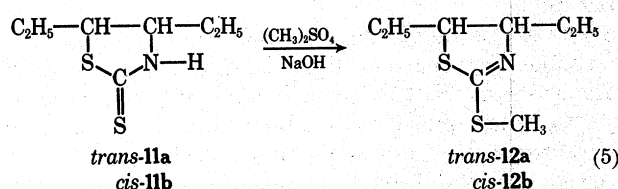


Figure 1.—Reaction of 2,3-dialkylaziridines with carbon disulfide.

achieved by use of dimethyl sulfate in alkaline medium (eq 5). Since this methylation reaction does not alter



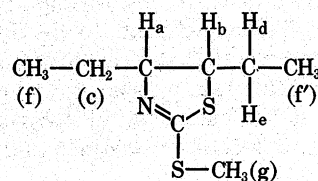
the stereochemistry of the starting thiazolidine-2-thiones, the trans isomer 11a will give 12a and the cis isomer 11b will give 12b.

The thiazoline derivatives 12a and 12b were obtained as liquids and were readily characterized by glpc, ir, and nmr. The gas chromatographic characteristics of thiazolines 12a and 12b are analogous to those observed in the oxazoline series^{11b} in that *cis*-thiazoline 12b has a longer relative retention time than the trans isomer 12a. Furthermore, it was found that the thiazoline 12b, obtained from 11b, contained ca. 8% of the isomeric thiazoline 12a. In the thiazoline 12a, none of the other isomer could be detected. These data would seem to indicate that the formation of thiazolidine-2-thiones from aziridines and carbon disulfide is a somewhat more stereoselective process when starting with *cis*-aziridines than with *trans*-aziridines.

The ir spectra of thiazolines 12a and 12b were characterized by an intense absorption at 1575 cm⁻¹, which

is ascribed to the C=N linkage of the thiazoline ring.¹³ This shift to lower frequency by ca. 80 cm⁻¹ from the normal C=N absorption is attributed to the electronic influence of the adjacent sulfur atoms.

The nmr spectra of thiazolines 12a and 12b were examined, and the same conclusion with regard to stereochemistry was reached, namely, that 12a has the *trans* geometry. For the *trans*-thiazoline 12a the observed methine coupling is 3.9 Hz while the *cis* coupling for thiazoline 12b is about 7.4 Hz. The complete spectra are given below. Mass spectral data for 12a and 12b yielded similar results as obtained for the starting thiones 11a and 11b in that the *cis* isomer 12b gives a P - 2 ion, not present in *trans*-12a, while the trans isomer has a larger percentage of the P - 29 ion than *cis*-12b.

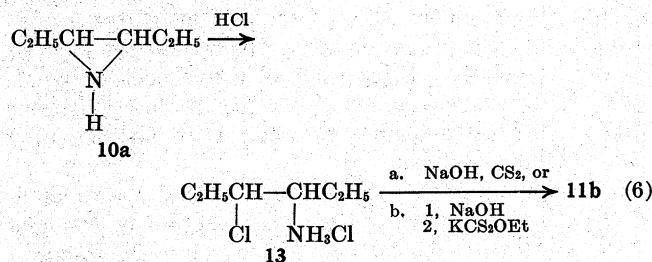


Nmr spectra of 2-thiazolines

<i>trans</i> -12a	<i>cis</i> -12b ^a
H _a , δ 4.05 (dt, J _{ab} = 3.9, J _{ac} = 6.4 Hz)	3.98 (m, J _{ab} = 7.4 Hz)
H _b , 3.78 (qd, J _{ba} = 3.9, J _{bd} = 6.0, J _{be} = 7.5 Hz)	3.76 (m, J _{ba} = 7.4 Hz)
H _{c-e} , 1.60 (m)	1.60 (m)
H _{f,f'} , 1.00 (m)	1.01 (t, J = 6.8 Hz)
H _g , 2.48 (s)	2.49 (s)

^a Coupling constant obtained from spin decoupling experiments.

Final confirmation of the above structural assignments was realized by the independent synthesis of the *cis*-thiazolidine-2-thione derivative 11b *via* the two methods outlined in eq 6.



The reaction of *cis*-2,3-diethylaziridine (10a) with hydrochloric acid gives the *threo*-β-chloroamine hydrochloride 13; this process is a typical S_N2 aziridine ring-opening reaction.¹⁴ The *threo*-β-chloroamine is converted, *via* an S_N2-type displacement of the β-chlorine atom, to the *cis*-thiazolidinethione isomer 11b by processes a^{15,16} or b.⁷ The thiazolidine-2-thione obtained *via* both procedures was identical in all respects with 11b obtained from *trans*-2,3-diethylaziridine and carbon disulfide (tlc, ir, and nmr), and by derivatization to the same 3-*p*-nitrobenzoyl and 2-methylthio-2-thiazoline derivatives.

In order to determine whether the size of the alkyl substituents on the aziridine ring in any way influenced

(13) W. Otting and F. Drawert, *Chem. Ber.*, **88**, 1469 (1955).

(14) O. C. Dermer and G. E. Ham, "Ethylenimine and Other Aziridines," Academic Press, New York, N. Y., 1969, p 208, and references listed therein.

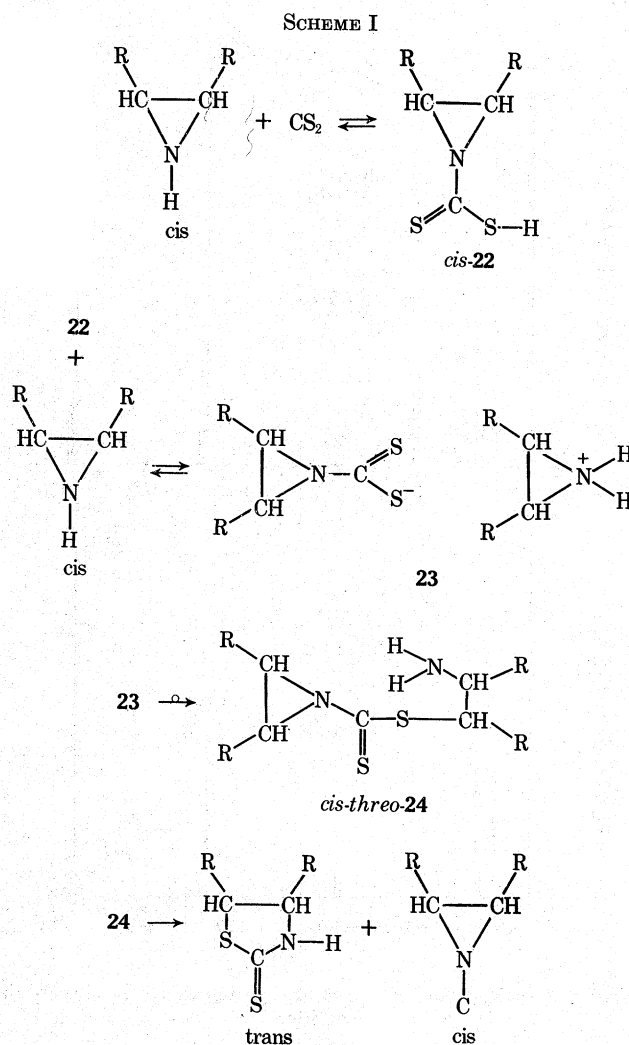
(15) M. Kojima, *Yakugaku Zasshi*, **79**, 11 (1959); *Chem. Abstr.*, **53**, 10185h (1959).

(16) V. I. Markov and S. I. Burmistrov, *Zh. Obshch. Khim.*, **35**, 153 (1965).

the stereochemical outcome of the reaction, the addition of carbon disulfide to *cis*- and *trans*-2,3-dioctylaziridine (14a and 14b) was investigated. As observed for the lower homologs, reaction of the *cis*-aziridine 14a with carbon disulfide yielded *trans*-4,5-dioctylthiazolidine-2-thione (15a) while the corresponding *trans*-aziridine 14b gave *cis*-4,5-dioctylthiazolidine-2-thione (15b) (eq 4). The structural assignments were made on the basis of elemental analyses, ir spectra, and molecular weight by mass spectrometry. The stereochemical assignments were made on the basis of the glpc retention times of the 2-methylthio-2-thiazoline derivatives (*trans* isomer elutes faster than *cis* isomer) and mass spectral fragmentation data. The reaction of methyl *cis*-8-(3-octyl-2-aziridinyl)octanoate (16) with carbon disulfide was also studied. The thiazolidine-2-thione 17 was obtained as a mixture of positional isomers as indicated by tlc. The conclusion to be drawn from the above experiments is that the size of the alkyl substituents on the aziridine ring appears to have no noticeable effect on the stereoselectivity of thiazolidine-2-thione formation from 2,3-dialkylaziridines and carbon disulfide.

In view of the difference in the orientation of ring opening in the reaction of 2-substituted aziridines with carbon disulfide, it was desirable to reinvestigate this aspect of the reaction with 2-alkyl-substituted aziridines. Toward this goal, the reaction of 2-octyl- and 2-decylaziridine (18 and 19) with carbon disulfide was studied (eq 4). In agreement with the earlier results of Clapp, *et al.*,³ it was found that the thiazolidine-2-thiones (20 and 21) derived from aziridines 18 and 19, respectively, were predominantly the 4-substituted isomers. The assignment of the alkyl substituent to the 4 position of the thiazolidine ring was made by an inspection of the nmr spectra. It has been found in the present study that for the thiazolidine-2-thione ring system, the chemical shift of the protons at the 4 position of the ring resonate at lower field than the protons at the 5 position. Integration of the respective signals gives the relative number of protons at these positions and readily distinguishes between 4- or 5-substituted thiazolidine-2-thiones.

It is apparent from the above data that the thiazolidine-2-thiones obtained from the reaction of *cis*- and *trans*-aziridines with carbon disulfide have the opposite configuration of the starting aziridine. With terminally substituted alkylaziridines, the three-membered ring is opened predominantly at the least substituted carbon atom. A proposed mechanism which accounts for this observed selectivity of inversion and orientation in aziridine ring opening is shown in Scheme I with a *cis*-aziridine as a prototype. The initial step requires the equilibrium formation of the aziridinyl dithiocarbamic acid 22 from the aziridine and carbon disulfide. Subsequent reaction of this dithiocarbamic acid with a second molecule of aziridine yields the intermediary aziridinium dithiocarbamate salt 23. Evidence for the formation of this intermediate has been found by Winternitz, *et al.*,⁷ and also in the present study. Attack of the dithiocarbamate anion at one of the carbon atoms of the aziridinium ion leads to the formation of the dithiocarbamic ester 24. This step of the reaction occurs *via* a nucleophilic S_N2 displacement of the nitrogen atom and is accompanied by inversion of configura-



tion. Thioester 24 then undergoes bond reorganization to yield the *trans*-thiazolidine-2-thione and the starting aziridine.

The above mechanism predicts that the reaction of aziridines with carbon disulfide should be a stereospecific process. With *cis*-aziridines a highly stereoselective reaction has indeed been observed, while with *trans*-aziridines a less stereoselective reaction has been observed. This difference in selectivity can be ascribed to steric retardation of the S_N2 ring opening of the aziridinium ion 23 when starting with a *trans*-aziridine. This retardation of nucleophilic attack allows for the competitive S_N1 ring opening of the *trans*-aziridinium ion 23 which subsequently leads to a mixture of geometric thiazolidine-2-thione isomers. With 2-alkyl-substituted aziridines, it is known that S_N2 type nucleophilic ring opening reactions¹⁴ occur predominantly at the least substituted carbon atom. Application of this mechanism to the present study predicts the formation of 4-alkyl-substituted thiazolidine-2-thiones, which have indeed been found to be the products of this reaction.

Experimental Section

Nmr spectra were obtained on a Jeolco CH-60 spectrometer. Chemical shifts are reported as δ (parts per million) relative to tetramethylsilane (TMS). The samples were run as 10% solutions in chloroform-*d*. Mass spectra were obtained on a CEC 110 spectrometer. Sample introduction was *via* the direct probe. Infrared spectra were obtained on a Perkin-Elmer Model 237

spectrometer. Glpc was carried out on a Hewlett-Packard Model-810 gas chromatograph. Melting points were determined in a capillary and are uncorrected.

Preparation and Purity of Aziridines.—The synthesis of the aziridines used in this study was carried out by either the iodine isocyanate or *N,N*-dichlorourethane route.^{17,18} Their purity and stereochemical integrity was shown to be >99% by gas-liquid (glpc) and thin layer chromatography (tlc) and by titration with perchloric acid.¹⁹

Preparation of Thiazolidine-2-thiones. Method A. General Procedure.—The aziridine (10 mmol) was added dropwise to carbon disulfide (5 ml) at ca. 5°. The addition is quite exothermic and must be controlled by external cooling. When the addition was complete, the mixture was heated to reflux for 20 min, and the excess carbon disulfide was then removed *in vacuo*. The crude thiazolidinethione was recrystallized from hexane or hexane-benzene. When the product separated as an oil, it was taken up in aqueous sodium hydroxide and reprecipitated by the addition of hydrochloric acid and chromatographed. Yield data and elemental analysis are listed in Table I.

Method B. General Procedure.—Carbon disulfide (5 ml) was placed into a Carius tube and cooled to ca. -80°. The aziridine (10 mmol) was then added dropwise, and the tube was sealed and heated to 100° for 6 hr. The tube was cooled to ca. -80° and opened to allow the hydrogen sulfide to escape. The contents was transferred to a flask and the excess carbon disulfide removed *in vacuo*. The thiazolidinethione was isolated as above. For yield data, see Table I.

***trans*-4,5-Diethylthiazolidine-2-thione (11a)** was prepared from *cis*-2,3-diethylaziridine. The pure product after recrystallization from hexane-ether had mp 59–60°; ir (neat) 3140 (NH), 2960, 1510 (CSNH), 1300, 1275, 1070, 1025 (C=S), and 960 cm⁻¹.

***cis*-4,5-Diethylthiazolidine-2-thione (11b)** was prepared from *trans*-2,3-diethylaziridine. Chromatography on Florisil (1/35) and elution with ether-benzene (4:96) gave the thiazolidinethione as a pale viscous oil: *n*_D²⁵ 1.5976; ir (neat) 3140 (NH), 2960, 1495 (CSNH), 1380, 1330, 1300, 1275, 1260, 1030 (C=S), and 970 cm⁻¹.

***trans*-4,5-Dioctylthiazolidine-2-thione (15a)** was obtained from *cis*-2,3-dioctylaziridine. Recrystallization from petroleum ether (bp 30–60°) gave the pure sample: mp 33.5–34.0°; ir (neat) 3140 (NH), 2920, 1500 (CSNH), 1460, 1375, 1275, 1030 (C=S), and 1010 cm⁻¹.

***cis*-4,5-Dioctylthiazolidine-2-thione (15b)** was obtained from *trans*-2,3-dioctylaziridine. Chromatography on Florisil²⁰ (1:30) and elution with benzene-hexane (1:3) gave the pure thiazolidinethione as a pale viscous oil: *n*_D²⁵ 1.5242; ir (neat) 3130 (NH), 2920, 1495 (CSNH), 1465, 1375, 1275, 1040, and 1020 cm⁻¹ (C=S).

4-Octylthiazolidine-2-thione (20) was prepared from 2-octylaziridine. Crystallization from hexane at -20° gave the pure adduct: mp 39–40°; ir (neat) 3140 (NH), 2960, 1500 (CSNH), 1275, 1030 (C=S), and 1010 cm⁻¹.

4-Decylthiazolidine-2-thione (21) was obtained from 2-decylaziridine. The pure thiazolidinethione was obtained by recrystallization from hexane at -20°: mp 59–60°; ir (KBr) 3160 (NH), 2910, 1575 (CSNH), 1330, 1135, 1115, 1050, 1020 (C=S), 930, 890, and 670 cm⁻¹.

***trans*-4(5)-Octyl-5(4)-(7-carbomethoxy)heptylthiazolidine-2-thione (17)** was prepared from *cis*-2-octyl-3-(7-carbomethoxy)heptylaziridine. The pure product was obtained as a mixture of positional isomers, mp 54–60°, after recrystallization from benzene-hexane: ir (KBr) 3110 (NH), 1740 (C=O), 1500 (CSNH), 1425, 1275, 1210, 1160, 1030 (C=S), 990, 920, and 875 cm⁻¹.

(17) C. G. Gebelein, G. Swift, and D. Swern, *J. Org. Chem.*, **32**, 3314 (1967).

(18) T. A. Foglia and D. Swern, *ibid.*, **32**, 75 (1967).

(19) G. Maerker, E. T. Haerberer, L. M. Gregory, and T. A. Foglia, *Anal. Chem.*, **41**, 1698 (1969).

(20) Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

2-Methylthio-*trans*-4,5-diethyl-2-thiazoline (12a).—Dimethyl sulfate (0.01 mol) was added in one portion to a solution of compound 11a (0.01 mol) in 5% NaOH (30 ml) at ca. 5°. The mixture was stored overnight and then extracted with ether (three 20-ml portions). The ether extracts were washed with H₂O (three 20-ml portions) and dried (Na₂SO₄), and the solvent was removed *in vacuo*. Distillation gave 1.2 g (63%) of thiazoline as a colorless liquid with bp 100–102° (0.1 mm): *n*_D²⁵ 1.5504; ir (neat) 2960, 1575 (C=N), 1375, 1310, 1180, 1125, 995, 940, and 820 cm⁻¹.

Anal. Calcd for C₈H₁₆NS₂: C, 50.8; H, 7.99; N, 7.40; S, 33.9. Found: C, 50.9; H, 8.12; N, 7.32; S, 33.6.

2-Methylthio-*cis*-4,5-diethyl-2-thiazoline (12b) was prepared from *cis*-thiazolidine 11b and dimethyl sulfate as described for the *trans* isomer: bp 98–99° (0.1 mm); *n*_D²⁵ 1.5497; ir (neat) 2960, 1570 (C=N), 1440, 1375, 1310, 995, and 945 cm⁻¹.

Anal. Calcd for C₈H₁₆NS₂: C, 50.8; H, 7.99; N, 7.40; S, 33.9. Found: C, 50.5; H, 8.07; N, 7.31; S, 33.7.

3-*p*-Nitrobenzoyl-*trans*-4,5-diethylthiazolidine-2-thione.—To a solution of *trans*-thione 11a (1 mmol) and triethylamine (1 ml) in benzene (10 ml) was added a solution of *p*-nitrobenzoyl chloride (1 mmol) in benzene (10 ml). The mixture was stirred for 1 hr at ambient temperature, the precipitate of triethylamine hydrochloride was filtered, and the filtrate was concentrated *in vacuo*. The residue was recrystallized from benzene-hexane (1:3) to give yellow crystals: mp 138.5–140°; yield 82%; ir (CHCl₃) 2960, 1680 (C=O), 1525 and 1350 (NO₂), 1305 (C=S), 1160, 1140, 1110, and 855 cm⁻¹.

Anal. Calcd for C₁₄H₁₆N₂O₃S₂: C, 51.8; H, 4.97; N, 8.63; S, 19.8. Found: C, 52.9; H, 5.07; N, 8.61; S, 19.7.

3-*p*-Nitrobenzoyl-*cis*-4,5-diethylthiazolidine-2-thione was obtained from *cis*-thione 11b as described for the *trans* isomer: mp 93–94°; ir (CHCl₃) 2960, 1680 (C=O), 1525 and 1350 (NO₂), 1305 (C=S), 1150, 1115, 1105, 1050, and 855 cm⁻¹.

Anal. Calcd for C₁₄H₁₆N₂O₃S₂: C, 51.8; H, 4.97; N, 8.63; S, 19.8. Found: C, 51.8; H, 5.21; N, 8.72; S, 19.6.

***cis*-4,5-Diethylthiazolidine-2-thione.**—To a solution of *threo*-3-amino-4-chlorohexane hydrochloride (0.03 mol) (obtained from the reaction of *cis*-2,3-diethylaziridine with concentrated HCl) and carbon disulfide (0.03 mol) in 50% ethanol (30 ml) was added a solution of NaOH (0.06 mol) in 50% ethanol (10 ml) at ca. 5°. After stirring overnight, the mixture was diluted with H₂O (50 ml) and extracted with ether (three 20-ml portions). The ether solution was extracted with 5% NaOH solution (two 20-ml portions) and the basic extracts were made acidic with concentrated HCl solution and extracted with ether (three 20-ml portions). The combined ether extracts were washed with H₂O (two 20-ml portions) and dried (Na₂SO₄), and solvent was removed *in vacuo*. The residue was chromatographed on Florisil to give 3.5 g (68%) of the thiazolidinethione, identical in all respects with 11b by tlc, ir, and nmr. Its 3-*p*-nitrobenzoyl derivative had mp 92–93° (the mixture melting point with the *p*-nitrobenzoyl derivative of 11b showed no depression). Alternatively this material was prepared by the following procedure. To a solution of 3-amino-4-chlorohexane (0.01 mol) in ethanol (25 ml) was added potassium ethyl xanthate (0.01 mol). The mixture was stirred overnight and the pure thiazolidinethione (80%) was obtained as above.

Registry No.—11a, 27932-05-4; 11b, 27787-21-9; 12a, 27787-22-0; 12b, 27787-25-3; 15a, 27787-26-4; 15b, 27787-27-5; 17, 27776-43-8; 20, 27784-25-4; 21, 27784-26-5; carbon disulfide, 75-15-0; 3-*p*-nitrobenzoyl-*trans*-4,5-diethylthiazolidine-2-thione, 27787-28-6; 3-*p*-nitrobenzoyl-*cis*-4,5-diethylthiazolidine-2-thione, 27787-29-7.

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